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(修正)

一、發明 名稱	中 文	燃燒前觸媒轉化器及此種轉化器之製法
	英 文	(A Pre-combustion Catalytic Converter and a Process for Producing Same)
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85100732 號專利申請案中文 請專利範圍修正本

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六、申請專利範圍

1. 一種燃燒前觸媒轉化器，其包括一種多孔性濾器，此濾器係至少部分以安定的金屬間化合物的觸媒調配物所製或是具有安定的金屬間化合物之觸媒調配物的塗層，該安定的金屬間化合物係包含錫與銻。
2. 根據申請專利範圍第 1 項之燃燒前觸媒轉化器，其中該錫原子組成係在 39.5% 至 57% 之範圍內。
3. 根據申請專利範圍第 1 項之燃燒前觸媒轉化器，其中該濾器具有孔隙度在 30% 至 50% 之範圍內。
4. 根據申請專利範圍第 1 項之燃燒前觸媒轉化器，其中該濾器具有透氣性為 $1 \times 10^{-13} \text{ m}^2$ 至 $400 \times 10^{-13} \text{ m}^2$ 。
5. 根據申請專利範圍第 1 項之燃燒前觸媒轉化器，其中該濾器具有孔隙，其大小範圍為 2 微米至 300 微米。
6. 根據申請專利範圍第 1 項之燃燒前觸媒轉化器，其中該濾器具有一種完整多孔性結構。
7. 一種供燃燒前觸媒轉化器用之濾器的製造方法，包括以下步驟：
製備一種安定的金屬間化合物之觸媒調配物，該安定的金屬間化合物係包含錫與銻；與
將該調配物製成多孔性濾器或將該調配物塗覆於多孔性濾器基材上。
8. 根據申請專利範圍第 7 項之製造方法，其中該調配物具有錫原子組成在 39.5% 至 57% 之範圍內。
9. 根據申請專利範圍第 7 項之製造方法，其中該濾器為一種藉下述方式所形成之完整多孔性結構：製備熔融體、將

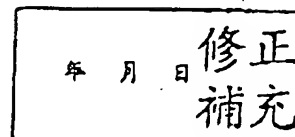
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Taiwan Patent Publication No. 374825



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(1995年) JUN 30 1995

"A Pre-combustion Catalytic Converter
and a Process for Producing Such a Converter"

Introduction

The present invention relates to a pre-combustion catalytic converter and to a process for producing such a converter.

5 It is well known to use a post-combustion catalytic converter to reduce noxious emissions from internal combustion engines. Typically, such converters have a honeycomb substrate of cordierite, which is a high-temperature ceramic. This substrate is plated with a catalyst of platinum material over a porous layer of aluminium oxide. Because of the expensive materials required and the complex structure, such converters are very expensive to produce. This is a major factor in limiting the spread of their use with consequent major adverse implications for the environment.

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Some pre-combustion catalytic converters have been described in the art. However, they do not appear to have been implemented to a significant extent in practice, partly because they are either not effective or are difficult and expensive to manufacture and maintain.

20

In the art, US 3682608 (Hicks) includes a very general description of catalysis of fuel before combustion for improved effectiveness. However, Hicks concentrates on the mesh structure for additional fuel-catalyzer contact and gives little detail of the catalysis.

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Some of the prior art describes use of a combination of tin, antimony, lead and mercury to provide an alloy which catalyses components of fuel for improved efficiency

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and/or reducing toxicity of the exhaust gases. However, these arrangements do not appear to be particularly effective. ZA 644782 (Broquet) describes use of this type of alloy in the form of pellets immersed in the fuel tank.

5 A pre-combustion catalytic converter having a platinum catalyst is described in US 5092303 (Brown). The catalyst is heated by an electric heater and causes cracking of liquid hydrocarbons in contact with it. It is not clear how effective the converter is, however, it appears to be
10 expensive to produce because of the materials used and the need for a heater and associated control devices.

Thus, while it has been apparent for some time that an effective pre-combustion catalytic converter would be desirable as it would be vastly less expensive and simpler
15 to install than post-combustion converters, heretofore they have not been used in practice because of lack of effectiveness for various reasons. This is causing ongoing environmental problems in most countries of the world. There is therefore an urgent need for an effective
20 pre-combustion converter. The invention is directed towards providing such a converter.

Statements of Invention

The invention provides a pre-combustion catalytic converter comprising a porous filter, formed at least
25 partially from or having a coating of a catalytic formulation of a stable intermetallic compound.

The filter may be mounted in a conventional fuel filter housing or alternatively in a housing for mounting in a fuel tank to complete the converter.

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In one embodiment, the filter comprises an alloy of tin and antimony.

Preferably, the tin atomic composition is in the range of 39.5% to 57%.

- 5 Preferably, the filter has a porosity in the range of 30% to 50%.

In another embodiment, the filter has a permeability of $1 \times 10^{-11} \text{ m}^2$ to $400 \times 10^{-11} \text{ m}^2$.

- 10 In a further embodiment, the filter has pores with sizes in the range of $2 \mu\text{m}$ to $300 \mu\text{m}$.

According to the invention, there is provided a process for producing a filter for a pre-combustion catalytic converter, the process comprising the steps of:-

- 15 preparing a catalytic formulation of a stable intermetallic compound; and

forming the formulation into a porous filter or coating the formulation onto a porous filter substrate.

- 20 When produced, the filter may be inserted in a conventional fuel filter housing, or alternatively in a housing for mounting in a fuel tank. As fuel passes through the filter, the molecules of fuel such as octane are chemically activated to cause more complete combustion with consequent reduced noxious exhaust emissions.

- 25 In one embodiment, the formulation comprises tin and antimony.

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In one embodiment, the formulation has a tin atomic composition in the range of 39.5% to 57%.

5 In another embodiment, the filter is an integral porous structure formed by preparing a melt, forming the melt into droplets, rapidly solidifying the droplets to form intermetallic particles, and subsequently bonding the particles. In this embodiment, an inert atmosphere is provided around the melt to prevent oxidation. The droplets may be formed by gas atomisation whereby an inert
10 gas breaks up a melt stream into the droplets. Nitrogen may be used for atomisation. The melt temperature is preferably below a level at which the melt becomes significantly reactive and absorbs and/or reacts with oxygen.

15 In one embodiment, the particles are bonded by sintering.

In the latter embodiment, the melt may comprise tin and antimony and the sintering may take place at a temperature in the range 300°C to 425°C for a time duration of 20 to 40 minutes.

20 In one embodiment, the sintering temperature is approximately 370°C and the time duration is approximately 30 minutes.

In a further embodiment, a pore forming agent is added prior to sintering. The agent may be stearic acid.

25 The formulation may include lead and/or bismuth.

In one embodiment, the filter is an integral porous structure.

- 5 -

In another embodiment, the filter is formed by deposition of the formulation onto a porous substrate.

Detailed Description of the Invention

5 The invention will be more clearly understood from the following description thereof given by way of example only with reference to the following drawings in which:-

Fig. 1 shows scanning electron micrographs of filter samples sintered in 100% nitrogen and 100% hydrogen atmospheres;

10 Fig. 2 is an X-ray diffraction pattern of sintered powder; and

Fig. 3 is an optical micrograph of the surface of filters.

15 Words which are used in headings of subsequent parts of the description are underlined.

In one example process of the invention, there is melt preparation in which an equiatomic composition of tin and antimony is melted in a graphite crucible using an induction heater. True atomic intermixing occurs in the molten state. The melt is held for 10 minutes at 500°C with a hydrogen gas cover to avoid oxidation.

20

The melt is bottom poured into an atomisation nozzle operated with high pressure nitrogen at a plenum pressure of 2.5 MPa for gas atomisation. Nitrogen escapes through an annular gap surrounding the melt stream, causing formation of droplets. The adiabatic expansion of the gas rapidly cools the droplets and accelerates them away from the melt source. During the subsequent flight, the

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droplets freeze into SbSn intermetallic crystalline particles with an average size of 10µm. The particles are collected in water and dried to form a powder.

5 The powder is subsequently loose packed into a machined graphite mould to form a disc with the addition of approximately 2% by weight stearic acid as a pore former. The graphite is heated in a hydrogen sintering atmosphere to bond the particles at 370°C for 30 minutes.

10 By sintering in this manner, a porous filter having an optimal balance between bonding and porosity is formed.

The filter is then mounted in a conventional fuel supply line filter housing to produce a pre-combustion catalytic converter. One such filter housing is described in US 3954625.

15 The filter has the following properties:-

porosity: 40-50%
permeability: 10^{-11}m^2
pore size: 25µm

20 The following description sets out alternative ways of implementing steps of the process.

Melt Preparation

25 The materials used could alternatively, or in addition, include other catalytic materials such as lead and/or bismuth to provide an alloy formulation. It is also envisaged that a small amount of platinum could be used. Where the formulation is SbSn, it need not be equiatomic. The end-product intermetallic must be stable and

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preferably has a tin atomic percentage in the range of 39.5 to 57%.

The melt may be at any temperature at which the melt does not absorb and/or react with oxygen.

- 5 It is envisaged that the materials need not necessarily be melted. For example, separate powders could be mechanically alloyed with sufficient energy such that the metals physically combine into a single powder.

- 10 Further, it is envisaged that a substrate having a porous structure may be used onto which the catalyst is coated, instead of providing an integral porous structure. In this case, a ceramic or metallic substrate may be used, and the catalyst may be coated by chemical or physical vapour deposition techniques, or by plasma spray coating.

- 15 Gas Atomisation

The gas atomisation pressure is dependent on the desired particle size, while being sufficient to provide the necessary high cooling rate. It is estimated that this is at least 10^3 °C/s.

- 20 For example, a lower pressure of 0.7 MPa may be used, providing a larger particle size of 20 µm.

The atomisation gas may alternatively be hydrogen, argon, helium or any other inert gas or any mixture of such gases.

- 25 Sintering Atmosphere

It is not essential that a hydrogen atmosphere be used.

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Due to the problems associated with using a lower temperature hydrogen furnace, sintering behaviour has been studied in nitrogen and nitrogen-hydrogen atmospheres. It was found that sintering of filters in either complete nitrogen or a combination of hydrogen and nitrogen atmospheres resulted in a black coating on the surface. This was due to the deposition of carbon on the surface of the filter. Stearic acid is a hydrocarbon consisting of several C-H bonds and was used as a pore-forming additive. Burn out of stearic acid is facilitated by the breaking of carbon-hydrogen bonds and the formation of simple gases using a reducing atmosphere. Hydrogen is a reducing atmosphere and helps in the burnout of stearic acid as well as in the sintering of the powders. The use of a nitrogen atmosphere does not cause these two processes because of its non-reducing behaviour. The carbon deposition on the surface also hampered the sinterability of the powders. The samples sintered using the hydrogen/nitrogen combination were black on the surface and were very fragile. The carbon coating was found only on the surface and not in the other sides of the filter.

An interesting phenomenon noticed was that when the powder samples were covered by a graphite plate over the mould during sintering, the carbon deposition was prevented. Also, the powders covered by the graphite plate and sintered in a nitrogen atmosphere showed the same sintering behaviour as the powders sintered in hydrogen atmospheres. The covering plate (which was made of graphite) would have caused the formation of carbon monoxide which is a reducing atmosphere. It is envisaged that a plate other than graphite could be used, provided some part of the mould is carbon when using a nitrogen atmosphere.

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Figure 1 shows fractographs of samples sintered in full hydrogen and full nitrogen atmospheres. They have a similar pore structure. The permeability, density and shrinkage of the filters sintered in 100% nitrogen and 100% hydrogen atmosphere are shown in Table 1.

Table 1

Atmosphere	Permeability (m ³)	Density (%)	% Shrinkage in ht.	% Shrinkage in dia.	% Mass Loss
100% H ₂	1x10 ⁻¹¹	58	20	11	3.3
100% N ₂	7x10 ⁻¹²	61	17	9.5	3.1

The X-ray diffraction patterns of the samples also show that the filters sintered using the nitrogen and hydrogen atmosphere form the same intermetallic phase SbSn (refer to Fig. 2).

In conclusion, powders mixed with 2 wt. % stearic acid showed the maximum permeability and pore size. The powders can be sintered in both 100% hydrogen as well as 100% nitrogen atmospheres, but for sintering in 100% nitrogen, the samples have to be covered at the top by a graphite boat to provide a reducing atmosphere. The samples sintered in 100% nitrogen atmosphere also formed the same intermetallic SbSn phase.

Sintering may be carried out by heating graphite to 370°C in a graphite boat arrangement. In this case, oxygen reacts with the graphite to form CO gas, further oxidation reactions leading to formation of CO₂. Both reactions remove oxygen or oxides from the sintering environment. There is a continual consumption of graphite as it is transformed into a vapour over time.

Any suitable reducing atmosphere could be used. Examples are use of methane, CO, H₂, N₂-H₂ mixes, NH₃, and dissociated ammonia. Suitable combinations of the above

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gases could be used by endothermic or exothermic burning processes. In particular, the use of H_2-N_2 is attractive because at low H_2 levels of a few percent, the atmosphere is non-explosive, yet still reducing.

5 Additional Step - Sintering Additives

The process may have the additional step of adding an additive to the intermetallic powder to dilate the pores during sintering to provide a larger catalyst surface area. This is briefly referred to above and is described
10 in more detail in this section.

In a specific example, stearic acid was chosen as a binder to be added to the powder to increase the permeability. The stearic acid used was Industrene 5016 manufactured by Witco. The reason for choosing stearic acid was that it
15 completely burns out before reaching the sintering temperature of $370^\circ C$. Stearic acid and the powder were mixed in a grinder to form a uniform blend of the powder and the binder. The total time of grinding was approximately 2 minutes. The grinding was done in short
20 time intervals of 20 seconds so as to prevent melting of stearic acid caused by heat generated in the grinder.

The sintering experiments were carried out in a retort in both nitrogen and hydrogen atmospheres. The permeability experiments were conducted using permeability measuring
25 equipment using air as the flow medium and mercury as the reference liquid in a column. The Archimedes method was used to measure the final density.

Table 2 below compares the ρ density and permeability of filters sintered by mixing powders with different weight
30 percentages of stearic acid at $370^\circ C$ in H_2 atmosphere.

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Table 2*

	Wt % binder	Permeability (m^2)	Pore diameter (μm)	Density (%)
5	0	5×10^{-13}	20	61
	0.5	9×10^{-13}	37	65
	1	9×10^{-13}	35	65
	1.5	7×10^{-13}	50	62
	2	2×10^{-11}	53	58

10 (* All the measurements were made for powders sintered in a cavity made of graphite boat, 19 mm in diameter and 4.3 mm in height and were not of the size of the actual filter).

15 The powder mixed with 2 wt.% stearic acid gave a maximum permeability of $2 \times 10^{-11} m^2$ and was approximately 50 times more permeable than the powder sintered without any binder. The powders mixed with 0.5 and 1 wt.% binder showed an increase in density while the powders mixed with 1.5 and 2 wt.% showed a decrease in density. Powders

20 mixed with stearic acid showed better sintering behaviour than the powders that were not mixed with binders. The initial increase in density could be attributed to this behaviour. The decrease in density for powders mixed with more than 1 wt.% was due to the excessive pores created by

25 the burnout of stearic acid. The powder mixed with 2 wt.% stearic acid and sintered had a maximum pore size of 52 μm and the highest porosity. Figure 3 shows the optical micrographs of the surface of filters sintered from powders with 0 and 2 wt.% stearic acid.

30 In general, any suitable agent which occupies space during heating but burns out during sintering may be used. Clean burnout at relatively low temperatures is desired. Stearic acid in powder form has been found to be suitable at a particle size of 100 μm or less. The powder may be

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added upon vibration of the intermetallic powder to allow a lower packing density, giving a dilated structure with a higher permeability after sintering.

5 Any suitable pore forming agent which has these general properties could be used, for example, ammonium carbonate, camphor, naphtha, ice, monostearates, and also low molecular weight waxes and organic gels.

10 It is also envisaged that a pore forming agent which acts to provide a reducing atmosphere could be used, for example paraffin wax, which forms methane on burnout.

The invention is not limited to the embodiments described. The filter could have physical properties which are different from those outlined above. The following are desirable parameter value ranges:-

15 porosity: 30 to 50%
permeability: 1 to 400 x 10⁻¹³ m²
pore size: 2 to 300 μm

20 The filter may be of any suitable type having a stable intermetallic compound of a catalytic metal formulation. Where the metals are tin and antimony only, the relative compositions may be varied within the range described above. Additional metals such as lead and/or bismuth may be used.

25 The process need not necessarily involve sintering. For example, the filter may be produced by melt spinning ribbon or wire and compressing it into filter form, in which case sintering may not be necessary.

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It is also envisaged that the filter could be formed from one or a number of layers so that the desired properties are obtained using the layers as "standard parts".

5 It will be appreciated that the invention provides a converter which may be used alone or in combination with a conventional post-combustion converter to dramatically reduce noxious emissions such as soot, hydrocarbons, and NO_x emissions. The following are some advantages of the converter of the invention:-

- 10 - it can be used for any fossil fuel burning engine,
- it is a direct substitute for conventional fuel filters,
- it catalyses the fuel and reduces exhaust emissions,
- 15 - it works in conjunction with post-combustion filters,
- the filter (and the case) are recyclable,
- it operates at the ambient temperature of the fuel, either in the tank or in the fuel supply
- 20 line.

第 85100732 號專利申請案之申請專利範圍修正本

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CLAIMS

1. A pre-combustion catalytic converter comprising a porous filter formed at least partially from or having a coating of a catalytic formulation of a stable intermetallic compound, comprising tin and antimony.
2. A pre-combustion catalytic converter as claimed in claim 1, wherein the tin atomic composition is in the range of 39.5% to 57%.
3. A pre-combustion catalytic converter as claimed in claim 1, wherein the filter has a porosity in the range of 30% to 50%.
4. A pre-combustion catalytic converter as claimed in claim 1, wherein the filter has a permeability of $1 \times 10^{-13} \text{ m}^2$ to $400 \times 10^{-13} \text{ m}^2$.
5. A pre-combustion catalytic converter as claimed in claim 1, wherein the filter has pores with sizes in the range of 2 μm to 300 μm .
6. A pre-combustion catalytic converter as claimed in claim 1, wherein the filter has an integral porous structure.
7. A process for producing filter for a pre-combustion catalytic converter, the process comprising the steps of:

preparing a catalytic formulation of a stable intermetallic compound, comprising tin and antimony; and

forming the formulation into a porous filter or coating the formulation onto a porous filter substrate.
8. A process as claimed in claim 7, wherein the formulation has a tin atomic composition in the range of 39.5% to 57%.
9. A process as claimed in claim 7, wherein the filter is an integral porous structure formed by preparing a melt, forming the melt into

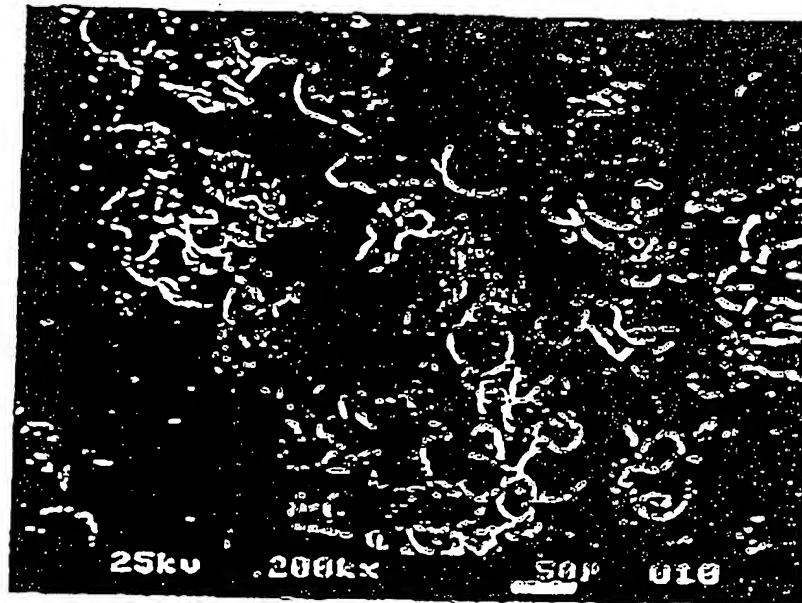
droplets, rapidly solidifying the droplets to form intermetallic particles, and subsequently bonding the particles.

10. A process as claimed in claim 7, wherein the formulation includes lead.
11. A process as claimed in claim 7, wherein the formulation includes bismuth.
12. A process as claimed in claim 7, wherein the filter is an integral porous structure.
13. A process as claimed in claim 7, wherein the filter is formed by deposition of the formulation onto a porous substrate.
14. A process as claimed in claim 9, wherein an inert atmosphere is provided around the melt to prevent oxidation.
15. A process as claimed in claim 9, wherein the melt temperature is below a level at which the melt becomes significantly reactive and absorbs and/or reacts with oxygen.
16. A process as claimed in claim 9, wherein the particles are bonded by sintering.
17. A process as claimed in claim 9 or 10, wherein the droplets are formed by gas atomisation whereby an inert gas breaks up a melt stream into the droplets.
18. A process as claimed in claim 11, wherein nitrogen is used for gas atomisation.
19. A process as claimed in claim 14, wherein the melt comprises tin and antimony and the sintering takes place at a temperature in the range 300 °C to 425 °C for a time duration of 20 to 40 minutes.
20. A process as claimed in claim 14, wherein a pore forming agent is added prior to sintering.

21. A process as claimed in claim 15, wherein the sintering temperature is approximately 370 °C and the time duration is approximately 30 minutes.
22. A process as claimed in claim 17, wherein the pore forming agent is stearic acid.
23. A pre-combustion catalytic converter whenever produced by a process as claimed in claim 7.

100% Hydrogen

1/3 (Formal)



100% Nitrogen

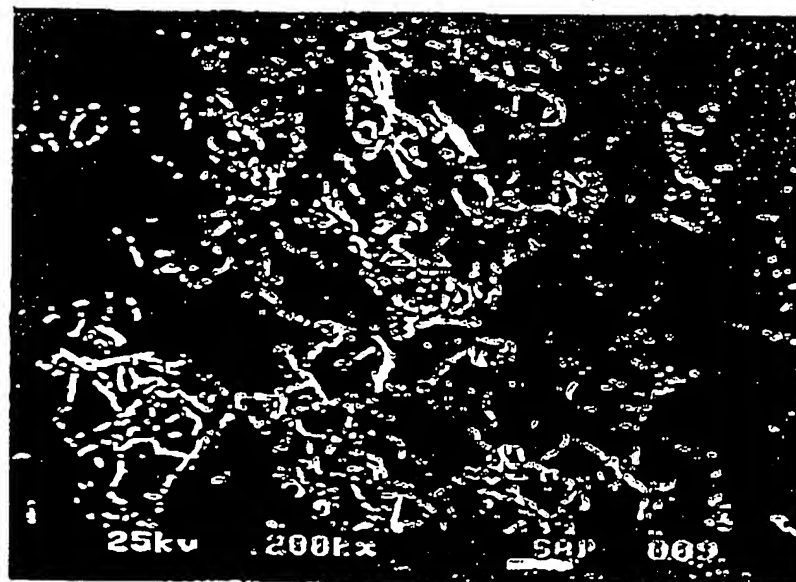


Figure 1: Scanning electron micrograph of samples sintered in 100% nitrogen and 100% hydrogen atmosphere

2/3 (Formal)

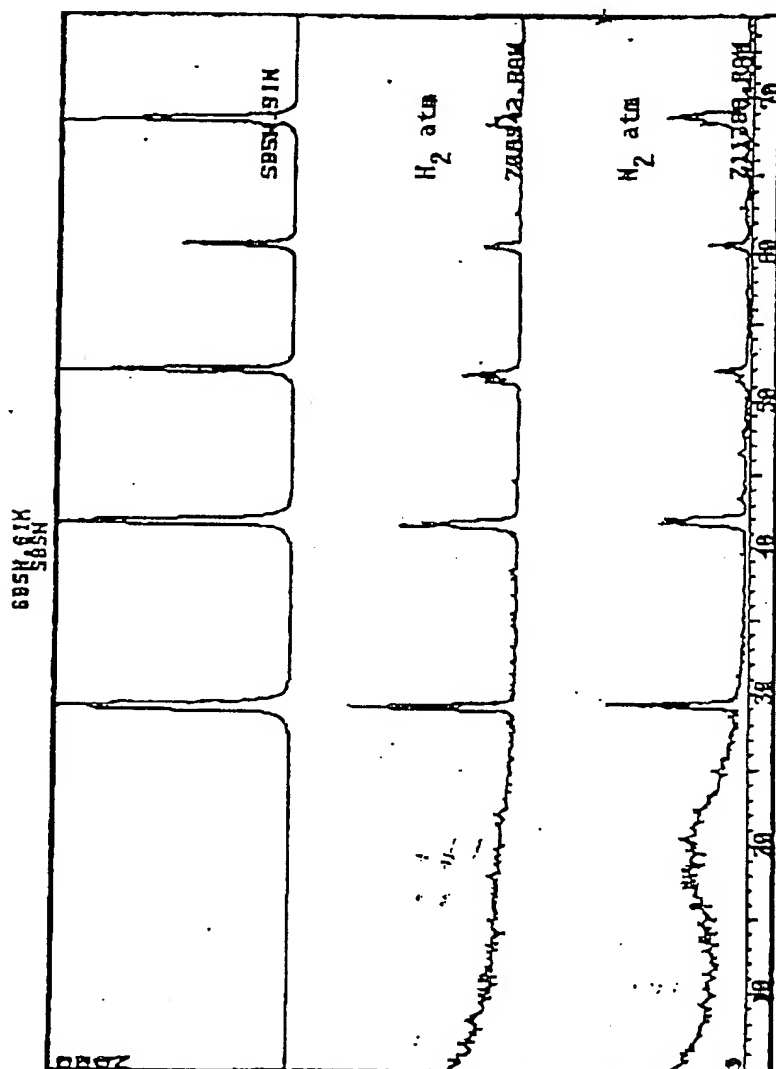
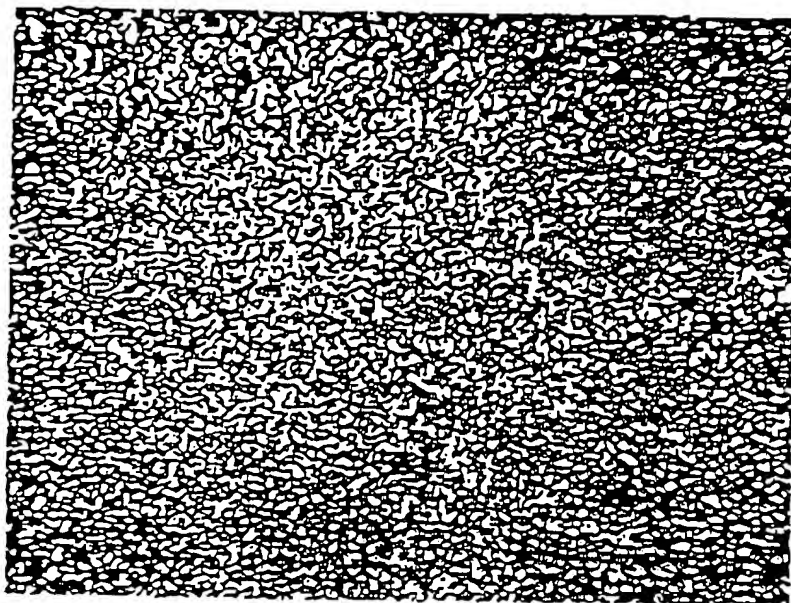


Figure 2: X-ray diffraction patterns of powder sintered in 100% H_2 and H_2 atm, compared with the standard Sb_3Sn

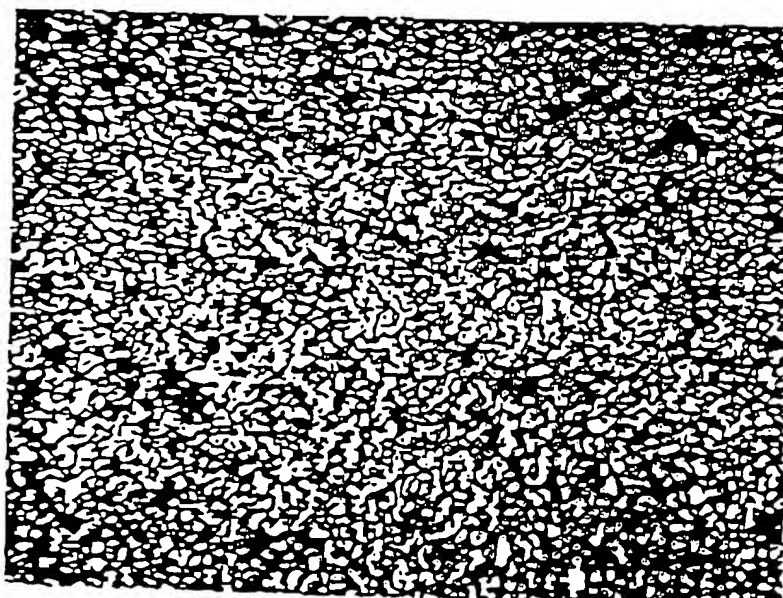
0 wt. % stearic acid

3/3 (Formal)



50x No Stearic Acid

2 wt. % stearic acid



50x with Stearic Acid (2wt %)

Figure 3: Optical micrographs of the surfaces of the filters sintered using powders mixed with 0 wt. % and 2 wt. % stearic acid

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